

Novel approach to zinc removal from circum-neutral mine waters using  
pelletised recovered hydrous ferric oxide

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## **Abstract**

Data are presented which evaluate the performance of a pilot-scale treatment system using pelletised hydrous ferric oxide (HFO; a waste stream from coal mine water treatment) as a high surface area sorbent for removing zinc (Zn) from a metal mine water discharge in the North Pennines Orefield, UK. Over a 10 month period the system removed Zn at mean area- and volume-adjusted removal rates of  $3.7 \text{ g m}^{-2} \text{ d}^{-1}$  and  $8.1 \text{ g m}^{-3} \text{ d}^{-1}$  respectively with a mean treatment efficiency of 32% at a low mean residence time of 49 minutes. There were seasonal effects in Zn removal owing to establishment and dieback of algae in the treatment tank. This led to increased Zn uptake in early summer months followed by slight Zn release upon algae senescence. In addition to these biosorptive processes, the principal sinks for Zn appear to be (1) sorption onto the HFO surface, and (2) precipitation with calcite-dominated secondary minerals. The latter were formed as a product of dissolution of portlandite in the cement binder and calcium recarbonation. Further optimisation of the HFO pelletisation process holds the possibility for providing a low-cost, low footprint treatment option for metal rich mine waters, in addition to a valuable after-use for recovered HFO from coal mine water treatment facilities.

## **Keywords**

Mine water, hydrous ferric oxide, remediation, zinc

## 1. Introduction

In river basins affected by historic metal mining, long-standing Zn pollution of surface waters can have significant impacts on ecology and pose a threat to compliance with surface water quality standards, such as those set out in Europe by the EU Water Framework Directive (2000/60/EC). In mining settings, Zn pollution arises principally due to the oxidative dissolution of sphalerite (ZnS) in both subterranean (e.g. mine shafts) and surface (e.g. waste rock heaps) settings and can be discharged to surface waters via a range of point and diffuse pathways (1). Although zinc is an essential trace element for plants and mammals (2), it can be toxic to sensitive aquatic life (e.g. salmonid fish) at low concentrations reflected in the maximum acceptable Zn concentration of  $8\text{-}125\mu\text{g L}^{-1}$  in the UK (hardness-dependent (as  $\text{mg L}^{-1} \text{CaCO}_3$ ) national environmental quality standard (EQS)).

Treatment options for Zn-rich mine waters are established for acidic mine waters where Zn is prevalent in the form  $\text{Zn}^{2+}$ . Here, active dosing with lime or caustic magnesia removes Zn as a hydroxide solid (3), while passive systems such as using a Dispersed Alkaline Substrate (DAS) of fine-grained alkaline material (e.g. calcite or caustic magnesia) on a coarse woodchip matrix have shown promise in laboratory and preliminary field trials (4). Alternatively, Zn can be immobilised as a sulphide in bioreactors where sulphate reducing bacteria are present in substrates usually comprising a mix of organic and calcareous alkalinity-generating media (e.g. Reducing and Alkalinity Producing Systems (RAPS); (5)). At circum-neutral mine

water discharges, which occur in many of the metal mining areas in the UK where mineral veins are hosted in Carboniferous strata (6), Zn is present predominantly as the complex  $\text{ZnCO}_3^0$ .  $\text{ZnCO}_3^0$  will not readily react to form non-carbonate solids. As such, attempts to employ aerobic passive treatment systems such as wetlands have not been very successful (3). Similarly, efforts to remove Zn as smithsonite ( $\text{ZnCO}_3$ ) using anoxic limestone drains to elevate to pH sufficient for  $\text{ZnCO}_3$  precipitation yielded only a 22% mean reduction in Zn during 3 month pilot-scale trials at Nenthead, Northumberland (7). While alkali dosing could be used in net alkaline waters, the comparatively high operating costs of this form of treatment preclude its deployment at most long-abandoned mine sites. Additionally, the nature of many metal mine waters, which discharge directly into rivers in steep-sided valleys where low gradient terrain is scarce, prompts the need for treatment technologies that have a small land 'footprint'. This demand limits the potential for wetland or RAPS-based treatment systems in many situations.

The use of low-cost, high surface area adsorbents such as zeolites (8), red mud (9), algae (10) and moss (11) for removing metals from waste water streams has been widely investigated in recent years. The effectiveness of these materials can vary greatly with factors such as pH, influent metal concentration, and local availability of these materials which affect their potential for widespread usage. The research presented here provides a pilot-scale evaluation of HFO pellets (locally called 'ochre') as a high surface area sorbent for removing Zn from metal mine discharges. The HFO pellets comprise poorly crystalline ferric oxyhydroxides (e.g.  $\text{Fe}(\text{OH})_3$  and  $\text{FeO}\cdot\text{OH}$  – (12)) which have been recovered from coal mine water treatment systems. HFO is a

major waste stream from coal mine water treatment facilities in the UK and Europe, with over 1200 tonnes of Fe recovered annually in the UK alone (13). Although several end uses for recovered HFO have been investigated and promising rates of removal of phosphorus from agricultural and sewage wastewaters have been documented (14), no single end use has so far been found to consume the current and projected supply of HFO in Europe. As such, large quantities are currently stockpiled pending disposal via landfill.

This current research builds on these developments to assess whether HFO is similarly effective as a sorbent for problematic metals (Zn in this case) from metal-rich discharges as it is for P. Widely cited literature (15) provides theoretical and laboratory-based indications of the effectiveness of hydrous ferric oxides as a sorbent for metals, particularly at the circum-neutral pH values encountered here. This is due in a large part to their high specific surface area and strong sorptive interactions with metal ions which adsorb through the formation of surface complexes. While these indications relate in large part to pure synthetic ferric oxides, laboratory studies that inform this current work have highlighted the potential for pelletised recovered HFO to effectively immobilize Zn and Pb from solution (16). Treatment efficiency in excess of 99% was found in continuous flow column experiments with influent concentrations of Zn and Pb at 3.0 and 2.5 mg L<sup>-1</sup> respectively. Zn and Pb removal was rapid, with >99% removed within a 2 hour contact time with surface sorption the dominant mode of removal from solution. The maximum Zn adsorption capacity of the pellets has also been estimated at 36.0 mg Zn g<sup>-1</sup> through batch experiments and observing breakthrough in continuous laboratory flow trials (16 and unpublished data of the authors). This compares favourably with other potentially low cost sorbents

such as blastfurnace slag (17.7mg Zn g<sup>-1</sup>; 17), red mud (12.6 mg Zn g<sup>-1</sup>; 17) and activated carbon (13.8mg Zn g<sup>-1</sup>; 18). This current study builds on the theoretical and laboratory background to assess whether the promising performance of pelletised recovered HFO as a Zn sorbent in laboratory studies is translated to field conditions in a pilot scale field trial at a polluting metal mine discharge. This will also assist in resolving the scale-dependence of geochemical processes occurring in treatment units between laboratory and field studies.

## **2. Materials and Methods**

### *2.1 Study site and pilot system set-up*

The North Pennines Orefield was mined intensively for lead (Pb), Zn and fluorspar between the 17<sup>th</sup> century and the 1970s. Despite the long timescales since abandonment of the majority of the mine facilities by the 1920s, several catchments draining the mineralised orefield continue to be afflicted by high dissolved Zn concentrations in breach of EQS (1, 19). The Scraithole mine water discharge emerges from the Scraithole Low Level (54 °49'01"N; 002°18'21"W) on the steep western bank of the River West Allen, Northumberland, UK. The set-up of the pilot treatment system is illustrated in Fig. 1. A small area of the bank was levelled off for the installation of the fibre glass treatment tank and header tank. A portion of the flow from the mine water discharge (which ranges between 0.6 and 3.5L s<sup>-1</sup>) was siphoned off using the header tank into the 2 cell treatment tank filled with approximately 180kg of HFO pellets. While the control valve aimed to ensure steady flow through the system, the flashy nature of the influent mine water meant that sporadically

increased turbulence in the header tank and flushing of fine sediments led to fall in flow rate as air bubbles were entrained in the feeder pipe. This led to inevitable changes in residence time which can be a common feature of pilot and full scale mine water treatment systems. The ability of treatment systems to accommodate such fluctuations is however important knowledge for engineering design. The HFO pellets comprised HFO recovered from a coal mine water treatment system at Acomb, Northumberland (54 °59'03"N; 002°06'59"W), which was air-dried in sludge beds prior to pelletisation with Portland cement (which comprises up to 25% volume of pellets). The pellets had a size range between 5 and 20mm diameter and an intra-granular porosity of 35%. This size of pellet was chosen after initial laboratory tests, which showed that while smaller sized pellets (<5mm diameter) provide a higher exposed surface area for adsorption, they required a greater volumetric binder component to overcome structural weakness. In addition, the smaller pellets had a lesser inter-granular pore space which increased the risk of system clogging. The pilot treatment tank had a total volume of 169L, which after the insertion of the HFO pellets left an active volume of 60L, and thus gives an inter-granular porosity of 36% in this current experimental set-up.

## *2.2 Sampling and analyses*

An Aquamatic Aqua Cell P2 with a 24 x 1L HDPE bottler autosampler was deployed to sample influent waters (in the header tank) and effluent waters from the treatment tank. These were set to sample every 12 hours and provide a continuous record over the 11 month trial of influent and effluent water quality. The samples from the auto-sampler were filtered (using 0.45µm cellulose nitrate filters) to remove

large debris, and then acidified with laboratory-grade nitric acid for subsequent cation analyses using a Varian Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Additionally, samples of both influent and effluent waters were taken on each sample visit every 10-12 days for full analyses. These samples consisted of on-site measurements of major physico-chemical parameters (pH, electrical conductivity, Eh relative to a H<sub>2</sub> electrode and water temperature) using a Myron L Ultrameter® calibrated on each sample day with pH 4, 7 and 10 buffer solutions and a 1413µS conductivity standard. Sample alkalinity was also assessed in the field using a two-stage titration against 1.6N H<sub>2</sub>SO<sub>4</sub> with phenolphthalein (to pH 8.3) and bromocresol green-methyl red indicators (to pH 4.6) to facilitate calculation of the constituents of sample alkalinity (i.e. hydroxyl, carbonate and bicarbonate alkalinity). For each sample, three polypropylene bottles were filled, one of which was acidified (for total cation and metal analysis), one of which was filtered (with 0.45µm cellulose nitrate filters) prior to acidification (for dissolved cation and metal analyses) and the other left untreated (for anion analysis). All samples were analysed (within one week of sampling) for major anion species using a Dionex 100 Ion Chromatograph and major cation and metals using ICP-OES. Replicate samples were taken periodically, rather than routinely, for logistical reasons, in accordance with Quality Assurance/Quality Control procedures detailed by APHA (20). Reliability of sample analyses was tested by charge balance calculations. An electro-neutrality within ±5% was considered to be of suitable accuracy. Selected hydrochemical data were analysed using the geochemical code PHREEQC v.1.5.10 (21) with the WATEQ4F database to calculate saturation indices (SI) of relevant mineral phases on a log scale. The flow rate through the tank was determined on each sample visit using a 1000mL measuring



cylinder and stopwatch. Flow rate was adjusted, where necessary using a tap fitted to the tank inlet (Fig. 1).

X-Ray Diffraction (XRD) analyses were performed on selected freeze-dried powdered samples of HFO and precipitated carbonate crusts using a PANalytical X'Pert Pro diffractometer (fitted with an X'Celerator) with a Cu-K $\alpha$  radiation source ( $\lambda=1.5406\text{\AA}$ ) at a scan speed of  $2.5\text{deg min}^{-1}$ . Phase identification was carried out by means of the X'Pert accompanying software program High Score Plus and the ICDD database, Sets 1-49 (22). Acid digestion was carried out on solid samples following the method detailed in (23), prior to ICP-OES analysis of digested samples. Solid samples were also analysed using a Hitachi S2400 Scanning Electron Microscope (SEM) fitted with an Oxford Instruments Isis 200 ultra thin window X-ray detector.

### **3. Results and Discussion**

#### *3.1 Water chemistry*

Summary physico-chemical data describing the composition of the Scraithole mine water and effluent water from the treatment tank during the course of the trial are presented in Table 1. The mine water displays hydrochemical facies typical of mine waters draining the North Pennine Orefield, with the dominant ions  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  (18, 24). Zn is present in concentrations between 0.4 and 2.2mg/L and the mine water is generally seen to be of consistent quality (hence relatively low standard deviation values for all parameters in Table 1). Occasional dilution of dissolved salts

in the mine water and corresponding enrichment of Al and Fe relate to high flow events when ingress of surface runoff from upland peat soils into the drainage adit dilutes the mine water prior to surface discharge. These runoff events also account for the changes in flow rate from baseflow at  $0.6\text{-}0.8\text{L s}^{-1}$  to peaks of  $2\text{-}3\text{L s}^{-1}$ .

The quality of the effluent waters is largely similar to the influent waters being dominated by  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  and total alkalinity (i.e.  $\text{HCO}_3^-$ , or  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  at higher pH - Table 1). Slight elevations in Fe (up to  $0.2\text{mg L}^{-1}$ ) in the effluent waters were apparent early in the trial and are associated with the washing of fines from the HFO pellets. Effluent Fe concentrations are not so high that they would be a regulatory concern (EQS value of  $1.0\text{mg/L}$  in dissolved fraction in the UK). The pellets also appear to be a slight source of  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$  and Al which are likely to be weathered from the HFO pellets. However, the main disparity between the influent and effluent waters is reflected in the pH. During the first 5 weeks of the trial (and for a short period over summer 2006), the effluent chemistry is characterised by elevated pH (up to pH 11.8), in excess of the surface water quality standard of pH 9 (Fig. 2). This is explicable due to the dissolution of portlandite in the cement binder, which produces the hydroxyl ion ( $\text{OH}^-$ ) and elevates solution pH (Eq 1). The elevated pH also leads to the rapid precipitation of calcite-dominated calcareous carbonate crusts as atmospheric  $\text{CO}_2$  is taken into the water column ultimately leading to the recarbonation of Ca (Eq 2). This phenomenon is similar to that apparent with the weathering of calcareous alkaline industrial residues, such as at steel slag disposal sites (25). While the influent waters are often supersaturated with respect to calcite, only occasionally do these SI appear sufficient for the heterogeneous precipitation of calcite (typically values  $>+0.3$  (26)). The effluent waters are consistently

supersaturated with calcite (mean  $SI_{\text{calcite}}$  of +0.86) throughout the trial due to the dissolution of the HFO pellet cement binder (see Fig. 2). These effects are particularly pronounced at the start of the trial with peak  $SI_{\text{calcite}}$  values of +1.51 recorded on 28/02/06, which is sufficient for the homogeneous precipitation of calcite from solution (26). High pH of this nature is clearly of concern for the quality of effluent waters immediately after establishment of the system. It is likely however that the problem could be overcome through: 1) pre-weathering / rinsing of the HFO prior to field-scale deployment, 2) using alternative binders such as Ca-silicate based cements, or 3) using lesser volumes of cement in the HFO pellet (which could be feasible at down to ~10% volume).



### 3.2 Metal removal and release

The overall pattern of Zn removal through the trial is presented in Fig. 3a and 3b. The residence time is also plotted alongside the influent and effluent Zn concentration curves in Fig. 3a; the system has a very low residence time, which varied between <10 minutes and 166 minutes with a mean residence time of 49 minutes.

There are a number of approaches to reporting, and therefore assessing, passive mine water treatment system performance. Treatment efficiency, the percentage reduction in contaminant concentration between influent and effluent (Eq 3), is the

simplest metric to apply, and is often reported. In the HFO drain system Zn removal varies between 73.8% and -13.0%, with a mean removal of 32% during the course of the trial (Fig. 3b).

$$\text{Treatment efficiency (\%)} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (3)$$

$C_i$  = influent contaminant concentration ( $\text{mg L}^{-1}$ );  $C_e$  = effluent contaminant concentration ( $\text{mg L}^{-1}$ )

However, treatment efficiency takes no account of flow-rate, and therefore residence time. For this reason area-adjusted removal rates are commonly reported for wetland systems, following the convention introduced by (27). This approach has far greater utility for meaningful assessment of both individual system performance and comparison between systems, since it quantifies system performance in the context of flow-rate (and therefore contaminant load) and system area. The calculation of area-adjusted removal rate is shown in Eq 4.

$$R_A = \frac{Q_d(C_i - C_e)}{A} \quad (4)$$

$A$  = treatment media area ( $\text{m}^2$ );  $Q_d$  = mean daily flow-rate ( $\text{m}^3 \text{ day}^{-1}$ );  $R_A$  = area-adjusted contaminant removal rate ( $\text{g m}^{-2} \text{ day}^{-1}$ ).

The area-adjusted removal rate is a logical approach for systems in which the length to width dimensions of a system are far higher than the depth dimension e.g. typically a wetland might be in the order of 100 m long and 50 m wide, but only 0.3 m deep. However, for systems such as the one reported here the depth is far more important (length : width : depth ratio in this case being approximately 1.0 : 0.6 : 0.8). Therefore it is arguably more appropriate to report results in units of *volume*-adjusted removal rate (by simply substituting volume ( $V$ ) for area ( $A$ ) in Eq 4). Table 2 compares

calculated performance metrics for this system with the contrasting passive treatment systems discussed by a number of other authors for various Zn-containing waste streams. Treatment efficiency and area-adjusted removal rate is calculated according to Eqs 3 and 4 respectively, for this system and those reported by other authors. Volume-adjusted removal rate is calculated using the modified version of Eq 4, as noted above. The data shown illustrate results for a range of systems, from laboratory-scale units (28, 29), through pilot-scale systems (this work, 28, 31), to full-scale treatment facilities (30, 32-34). There are of course difficulties in comparing between units of different sizes, due to scale-dependence phenomena in water treatment systems, and differences in environmental conditions. Nevertheless, the mean area-adjusted removal rate ( $3.7 \text{ g m}^{-2} \text{ d}^{-1}$ ) and volume-adjusted removal rate ( $6.2 \text{ g m}^{-3} \text{ d}^{-1}$ ) of this system are substantially higher than the other systems, for which the highest area-adjusted and volume-adjusted removal rates are  $0.47 \text{ g m}^{-2} \text{ d}^{-1}$  and  $1.4 \text{ g m}^{-3} \text{ d}^{-1}$  respectively. This is despite the below average treatment efficiency of the HFO drain system (32%), and illustrates the limitations of treatment efficiency as a performance metric.

The very encouraging area- and volume-adjusted removal rates evident for this system, coupled with the short residence time, suggest that the use of iron HFO as a sorptive media for the remediation of Zn-contaminated mine waters, and other metalliferous waste streams, should be pursued further. Although such treatment technologies would not provide the ancillary benefits of wetlands (e.g. potential wildlife habitat) the small footprint, and efficient treatment performance per unit area and volume, indicate that these units could provide a genuine passive treatment option for waste streams in regions where land availability is limited. Furthermore, the

notion of using one waste material to treat another waste stream is clearly attractive on sustainability grounds.

Notwithstanding this promising performance of the pilot-scale unit, further development of the technology will be required, and this principally relates to consistency of medium- to long-term performance. A strong seasonal pattern in Zn removal is apparent over the trial period (Fig 3a and 3b). The first three months are characterised by a fairly consistent treatment efficiency (36.6%; standard deviation:  $\pm 7.1$ ) and volumetric removal rate ( $R_v$ :  $5.3 \text{ g Zn m}^3 \text{ day}^{-1}$ ; standard deviation:  $\pm 1.3$ ). Performance improves to a mean treatment efficiency of 59.0% (s.d.:  $\pm 12.8$ ) during June and July with a mean  $R_v$  of  $22.9 \text{ g Zn m}^3 \text{ day}^{-1}$  (s.d.:  $\pm 10.1$ ) over the period (Fig. 3b). The influent and effluent Zn concentration curves then converge in August until the effluent Zn concentration exceeds the influent for two short periods in August and September. During this period treatment efficiency falls markedly to a mean of 7% (s.d.: 4.8), with similarly poor mean  $R_v$  values of  $1.9 \text{ g Zn m}^3 \text{ day}^{-1}$  (s.d.: 2.8). From October onwards the effluent Zn concentrations diminish and Zn treatment efficiency returns to fairly consistent values with a mean of 25.4% (s.d.:  $\pm 11.0$ ) mean  $R_v$  of  $5.6 \text{ g Zn m}^3 \text{ day}^{-1}$  (s.d.: 1.9). The seasonality in removal patterns appears to be explicable due to the effects of spontaneous establishment and dieback of algae in the treatment tank. The increased removal rate in June and July corresponds with the establishment of the green algae *Mugeotia* spp. and *Stigeoclonium tenue* in the tank. These taxa are ubiquitous to surface waters in the North Pennines area of the UK due to their tolerance of Zn-rich conditions (35) and have been shown to uptake Zn from surface waters during the growing season (36). The dieback of the algae occurred between

August and October when Zn in the effluent waters occasionally exceeded influent concentrations, suggesting release of Zn from the decaying algae. After the dieback, the Zn treatment efficiency falls slightly relative to performance early in the trial suggesting possible loss of adsorption capacity over time as would be expected. However, mean  $R_v$  values during the latter four months of the trial are slightly higher than in the early stages of the trial. While the adsorption capacity of the pellets does not appear to be reached during the trial, underlining the promise for longevity of performance, further field tests (either longer-term or at higher Zn loading rates) are required to determine the maximum adsorption capacity of the pellets under field conditions. This will permit accurate quantification of HFO pellet longevity and thus aid in full life-cycle cost estimates for the technology.

To avoid the release of zinc between August and October, due to seasonal dieback of algae, a number of alternative strategies may require investigation, such as complete burial of the system (to prevent light penetration), or installation of a temporary secondary treatment unit during algal dieback. The overall issue of the extent and frequency of waste disposal is an important consideration for any new treatment technology. In this respect, it should be borne in mind that the HFO pellets are produced from a waste material. In the absence of a suitable market for re-use, the HFO is already disposed of to landfill in the majority of cases (in the UK at least). Therefore there would be no actual *additional* waste disposal burden in the context of an holistic view of the environmental management of mining and metalliferous waste streams, as long as the zinc was confirmed to be immobile in the environment of the disposal repository.

Outside the influence of the algae colonisation and dieback in the tank, there are several other factors that could influence the Zn removal rate. Zn removal was correlated with effluent water pH, water temperature, residence time and influent Zn concentration to assess whether there were any other clear relations between these factors and the performance of the HFO pellets. Table 3 shows there are no strong correlations between any of the variables. However, there is a significant (at the 0.05 level) positive correlation between Zn removal and influent Zn concentration and a significant negative correlation between Zn removal and total alkalinity. The reason for the latter is unclear, although many of the high alkalinity values were recorded early in the trial (when pH was high) when Zn removal was relatively low compared to the peak summer values. The correlation between removal and influent Zn does suggest that the effectiveness of the HFO pellet media could well be increased at sites with higher influent Zn concentrations. Laboratory studies suggest that the HFO pellets can remove significant (i.e. >95% influent) quantities of influent Zn up to concentrations of 15mg/L, albeit at higher residence times (<10 hours) ((16) and unpublished data of the authors).

Concentrations of As, Cr, Ni and Pb were found to be below detection limits in all effluent samples (see Table 1), suggesting that the HFO and the binding cement are not significant sources of the above metals. This is important for assessing the feasibility of using HFO pellets as a treatment media, given the presence of these metals in the cement binder and HFO itself (Table 4).

### *3.3 Solid analyses*



Elevated pH in the effluent water led to the precipitation of calcareous carbonate crusts on the edge of the treatment tank and on the surface of the HFO in places. These crusts were analysed using XRD and were found to be predominantly calcite, with an identifiable, but less intense aragonite signature (Fig. 4b). Geochemical modelling also predicted the presence of several other phases which were at least occasionally supersaturated in the effluent waters (Table 5). These phases include the above  $\text{CaCO}_3$  species but also a range of Zn, Mg and Fe oxide and hydroxide phases. Some of the species detailed in Table 5 were predicted to be supersaturated only in the early stages of the trial when peak saturation index values were recorded and effluent pH (and thus  $\text{OH}^-$ ) was elevated (e.g. for brucite ( $\text{Mg}(\text{OH})_2$ ) and amorphous zinc oxide ( $\text{ZnO}$ )). XRD analyses were also undertaken on the HFO samples (see Fig. 1 for sample locations) to determine whether any of these other crystalline phases were present on the HFO surface. Table 5 and Fig. 4b highlight that only calcite was confirmed present by XRD on any of the HFO samples. While this does not rule out the presence of the other phases predicted by geochemical modeling, which may have occurred at trace quantities not detectable by XRD, it does highlight calcite as the dominant secondary precipitate occurring in the treatment system.

This precipitation of secondary minerals was seen to be of significance for Zn removal. The co-precipitation of divalent metals on calcite is well documented (37), and it appears that calcite produced in the treatment tank served as a significant sink for Zn. The composition of digested solid samples of (1) HFO (sample codes 1a-c and 2a-c), (2) control HFO samples (OCC: representing the condition of the HFO pre-immersion) and (3) carbonate crust (calcite) from the tank wall (SC1) are presented in Table 5. The carbonate crust sample taken from the wall of the tank (sample SC1) has

Zn content higher than any of the HFO samples at 3270mg/kg. The composition of the carbonate precipitates on the treatment tank wall reveals significant quantities of Mg, Mn, Na, Si, and Ba in addition to Ca and Zn, which also suggests the uptake of these elements in the secondary precipitates.

The Zn content of the HFO pellets varies between 430mg kg<sup>-1</sup> and 2070mg kg<sup>-1</sup>. The higher Zn values are found in the surface layers of the HFO pellets (samples 1a and 2a – see Fig. 1). This may be related to the widespread presence of biofilms and algae on the surface layers, which were less abundant in the middle and basal HFO samples. These concentrations fall an order of magnitude below the estimated laboratory adsorption capacity of the media (36.0 mg Zn g<sup>-1</sup>) suggesting that either the adsorption capacity was not reached during the trials or there was a loss of porosity of the media associated with biofilm and secondary precipitate formation, which may limit adsorption capacity in field situations. SEM imaging of the HFO surface shows the nature of the Zn sink to be evenly distributed across the HFO pellet surface and not associated with any locus of surface crystallisation (Fig. 5), suggesting surface sorption to be the dominant Zn removal mechanism.

### *3.4 Future studies*

Future studies should: (1) assess metal removal rates at varying residence times and over longer time scales to determine the longevity and permanence of metal sorption on the HFO, (2) trial alternative HFO pellet compositions, such as using Ca-silicate based cement binder and minimising the volume of binder used to limit the problems

with elevated effluent pH, (3) assess metal removal rates at other metal-rich discharges, which should encompass not only metal mine waters with higher influent metal concentrations, but also at other metal-rich discharges (e.g. industrial effluents, highways runoff) and (4) appraise the engineering design of such systems and undertake rigorous cost-benefit analyses of the technology compared to other treatment options once full-scale production of the pellets is possible.

#### **4. Conclusions**

1. This study has highlighted the potential for using a waste stream generated from coal mine water treatment to be developed as a low-cost, small footprint treatment option for circum neutral metal mine waters. The pilot-scale field trials showed the HFO pellet drain to have a mean treatment efficiency of 32%, at an average residence time of 49 minutes.

2. However, more instructive insight as to the performance of the system can be gained from the area- and volume- adjusted removal rate. With a mean area-adjusted removal rate of  $3.7 \text{ g/m}^2/\text{d}$  and volume-adjusted removal rate of  $8.1 \text{ g/m}^3/\text{d}$  the HFO drain system proves substantially more effective than many alternative passive units for Zn removal.

3. Elevated pH in the effluent waters early in the trial was ascribable to dissolution of the cement binder which leads to the formation of secondary calcite-dominated crusts on the HFO surface and treatment tank walls. The Zn removal on the HFO pellets and secondary precipitates appear to be supplemented by biosorptive / microbial processes relating to the colonisation of algae in the tank over summer months. The dieback of the algae does lead to short periods of time when the system is a net-exporter of Zn

and holds clear issues for the design of full-scale remediation systems, albeit mitigating engineering measures may be feasible.

4. The overall Zn removal rates documented here do show considerable promise for further development of HFO pellets as a treatment media for metal rich discharges. Future research should continue to optimize the process through assessing alternative binder materials and quantifying important performance parameters (removal rates, efficiency, maximum adsorption capacity) at a range of Zn polluting effluents.

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## Table Legends

Table 1. Hydrochemical composition of the Scraithole minewater (IN) and effluent water from the treatment tank (OUT). All values in  $\text{mg L}^{-1}$  except pH, water temperature ( $^{\circ}\text{C}$ ), specific conductance ( $\mu\text{S}$ ),  $Eh$  (mV), total alkalinity ( $\text{mg L}^{-1}$  as  $\text{CaCO}_3$ ). Data displays mean, standard deviation (St. dev.) and maximum over the sample period.  $n = 24$  for in and out.

Table 2. Treatment system performance of HFO drain compared to other passive treatment technologies, using various assessment metrics and mean values (figures derived where not explicitly given in text of references)

Table 3. Pearson's two-tailed correlation matrix for various parameters.

Table 4. The major and minor elemental composition of digested samples taken from the treatment tank. See Fig. 1 for sample locations. All values in  $\text{mg kg}^{-1}$ .

Table 5. Solid phases predicted in the influent (IN) and effluent (OUT) waters from the treatment tank by geochemical modelling and confirmed presence of crystalline phases by XRD ('+' denotes presence). Data show mean and maximum values ( $n = 14$ ) of saturation indices on a log scale.

### Figure legends

Fig. 1. Schematic diagram showing the set up of the pilot treatment tank.

Fig. 2. Water pH variation during the trial in influent (pH IN) and tank effluent (pH OUT) waters. Fig. S1b. Saturation index for calcite ( $SI_{\text{calcite}}$ ) variation during the trial in influent (SI calcite IN) and effluent (SI calcite OUT) waters.

Fig. 3. Mean daily zinc concentrations in influent and effluent waters alongside mean daily residence time during the trial.

Fig. 4. XRD spectrum for secondary precipitates recovered from the wall of the treatment tank showing the presence of calcite and aragonite (4a). XRD spectrum for powdered, weathered HFO from the treatment tank at the end of the trial highlighting the presence of calcite (4b).

Fig. 5. SEM image of HFO pellet surface highlighting the poorly crystalline HFO surface (A) and the even distribution of Zn (shown as false colour using energy dispersive X-ray analysis) across the HFO surface (B).

Table 1

Determinand	IN			OUT		
	Mean	St. dev.	Max	Mean	St. dev.	Max
pH	7.8	0.5	8.5	8.7	1.1	11.9
Temperature	7.3	3.2	12.6	6.1	2.4	9.4
Specific conductance	589.3	187.1	770.0	631.7	393.2	747.5
<i>Eh</i>	107.3	31.7	154	155.1	47.5	217.0
Major ions						
Ca	68.7	20.8	86.1	71.9	12.0	88.8
Mg	14.8	5.2	18.9	13.5	3.9	17.5
K	5.9	2.9	9.0	6.7	2.8	10.2
Na	32.1	13.4	48.1	29.3	9.4	37.3
Cl	7.6	2.2	11.5	8.5	3.9	18.0
SO <sub>4</sub>	119.1	49.5	175.4	138.4	23.3	173.0
Total Alkalinity	163.9	57.0	226.0	156.0	40.3	210
Metals						
Al	<0.05	-	0.30	0.056	0.037	0.10
As	<0.01	-		<0.01	-	
Cd	<0.01	-	<0.01	<0.01	-	<0.01
Cr	<0.01	-	<0.01	<0.01	-	<0.01
Fe	<0.1	-	0.5	0.13	0.12	0.35
Mn	<0.05	-	0.1	0.05	0.02	0.07
Ni	<0.01	-	<0.01	<0.01	-	<0.01
Pb	<0.05	-	<0.05	<0.05	-	<0.05
Si	2.9	1.1	4.8	1.7	1.6	3.9
Zn	1.5	0.5	2.2	0.9	0.3	1.5

Table 2.

Wastewater type	System type	Monitoring period (months)	Area (m <sup>2</sup> ) Volume (m <sup>3</sup> )	Flow (L s <sup>-1</sup> )	Residence time (days)	Zn influent / effluent (mg L <sup>-1</sup> )	Load removed (g d <sup>-1</sup> )	Treatment efficiency (%)	Area-adjusted removal rate (g m <sup>-2</sup> d <sup>-1</sup> )	Volume-adjusted removal rate (g m <sup>-3</sup> d <sup>-1</sup> )
Mine water	Pilot-scale HFO drain	10	0.35 m <sup>2</sup> 0.16 m <sup>3</sup>	0.03	0.034	1.7 / 1.2	1.30	32	3.71	8.13
Mine water <sup>(30)</sup>	Pilot-scale Aerobic wetland / algal mat	48	420 m <sup>2</sup> 240 m <sup>3</sup>	0.04 – 0.17	16 - 79	16 / 1.2	191.8	91	0.47	0.80
Mine water <sup>(30)</sup>	Full-scale aerobic wetland / algal mat	24	13200 m <sup>2</sup> 6000 m <sup>3</sup>	8.5	8.2	14.4 / 9.9	3,300	31	0.25	0.55
Mine water <sup>(31)</sup>	Pilot-scale Anoxic Limestone Drain	1.5	4.5 m <sup>2</sup> 2.25 m <sup>3</sup>	0.02	0.65	6.91 / 5.74	2.02	17	0.45	0.90
Not specified <sup>(32)</sup>	Subsurface flow wetland	-	- -	-	-	2.50 / 0.73	-	71	0.11	-
Urban runoff <sup>(34)</sup>	Full-scale Surface flow wetland	12	8250 m <sup>2</sup> -	18	-	0.065 / 0.057	12.4	12	0.002	-
Domestic wastewater <sup>(33)</sup>	Full-scale Gravel subsurface flow wetland	9	650 m <sup>2</sup> 325 m <sup>3</sup>	6.25	-	0.113 / 0.014	53.5	88	0.08	0.16

Zn-containing wastewater <sup>(28)</sup>	Lab-scale wetland	Hydrosoil surface	2	0.896 m <sup>2</sup>	0.003	1.00	1.76 / 0.34	0.319	81	0.37	1.42
				0.224 m <sup>3</sup>			1.76 / 0.52	0.278		70	0.31
Smelter water <sup>(29)</sup>	Lab-scale wetland	subsurface	4	0.231 m <sup>2</sup>	8.3 x 10 <sup>-5</sup>	7.00	0.140 / 0.043	7 x 10 <sup>-4</sup>	69	0.003	0.01
				0.069 m <sup>3</sup>							

Table 3.

	Zn removal	Residence time	pH	Temperature	Total Alkalinity	Influent Zn
Zn removal	-	0.117	0.256	0.174	-0.454*	0.472*
Residence time	0.117	-	0.394*	0.005	0.124	0.068
pH	0.256	0.394*	-	-0.186	0.045	-0.197
Temperature	0.174	0.005	0.186	-	-0.280	0.393*
Total Alkalinity	-0.454*	0.124	0.045	0.280	-	-0.240
Influent Zn	0.472*	0.068	-0.197	0.393*	0.240	-

\* denotes significant correlation at the 0.05 level (two-tailed)

Table 4.

Determinand	1a	1b	1c	2a	2b	2c	SC1	OCC
Major elements								
Ca	302432	285312	307321	308549	296353	311134	409334	203440
Mg	5384	4510	6073	4773	5072	5073	35130	4998
K	465	380	426	758	412	423	87	469
Na	1895	1832	1738	1940	1876	1893	3748	1798
Fe	89065	83358	85263	93696	89187	89314	193	15644
Al	6620	5082	7083	6923	6232	6393	1631	6023
Minor elements								
As	3.0	3.1	4.5	4.2	3.7	4.2	<LOD	3.5
B	52.8	54.0	580	54.5	65.3	55.9	2.1	54.9
Ba	73.1	75.6	69.6	156.3	73.1	71.2	201	79.8
Cd	2.3	2.1	1.6	2.4	2.2	1.9	3.2	2.0
Cr	8.6	6.2	10.3	9.5	7.9	8.7	0.2	8.9
Cu	6.4	6.1	8.7	8.0	6.7	8.7	0.9	7.2



Mn	559.2	513.9	519.5	656.8	547.5	525.2	1616	685.8
Mo	1.5	1.2	1.8	1.6	1.6	1.5	0.4	1.9
Ni	20.8	19.9	18.8	23.8	20.8	19.2	24.1	21.8
Pb	10.4	8.1	9.8	14.7	1.8	9.4	8.7	10.2
Si	236	291	323	348	223	231	1918	276
Sr	3802	3648	3661	3913	3771	3891	1300.7	3828
V	9.4	7.1	9.9	9.7	8.9	9.0	<LOD	8.5
Zn	1824	1314	430	1763	1071	842	3270	87

Table 5.

Species	<u>IN</u>		<u>OUT</u>		Presence confirmed by XRD?
	Mean	Maximum	Mean	Maximum	
Aragonite (CaCO <sub>3</sub> )	-0.11	0.8	0.70	1.35	
Artinite (Mg <sub>2</sub> (CO <sub>3</sub> )(OH) <sub>2</sub> ·3H <sub>2</sub> O)	-7.64	-4.9	-4.64	1.57	
Brucite (Mg(OH) <sub>2</sub> )	-5.98	-4.2	-3.81	1.69	
Calcite (CaCO <sub>3</sub> )	0.06	0.96	0.86	1.51	+
Dolomite (CaMg(CO <sub>3</sub> ) <sub>2</sub> )	-0.99	0.79	0.54	1.71	
Fe(OH) <sub>2</sub> ·7ClO <sub>3</sub>	4.96	5.87	6.41	7.69	
Fe(OH) <sub>3</sub> (a)	0.49	1.48	2.34	3.52	
Fe <sub>3</sub> (OH) <sub>8</sub>	-0.30	1.95	3.19	7.14	
Goethite (FeOOH)	5.64	6.78	7.49	8.72	
Hematite (Fe <sub>2</sub> O <sub>3</sub> )	12.20	15.48	16.90	19.35	
Maghemite (Fe <sub>2</sub> O <sub>3</sub> )	4.37	6.36	8.21	10.43	
Magnesite (MgCO <sub>3</sub> )	-1.09	-0.08	-0.27	0.38	
Magnetite (Fe <sub>3</sub> O <sub>4</sub> )	13.62	16.35	17.45	21.22	
Quartz (SiO <sub>2</sub> )	-0.09	0.13	-0.16	0.05	
Smithsonite (ZnCO <sub>3</sub> )	-0.88	-0.33	-1.79	-0.53	
Willemite (Zn <sub>2</sub> SiO <sub>4</sub> )	-0.68	2.05	-0.85	0.32	
ZnO(a)	-0.99	0.06	-0.52	-0.08	
ZnCO <sub>3</sub> ·H <sub>2</sub> O	-0.41	0.09	-0.34	0.08	

ZnSiO<sub>3</sub>

2.14

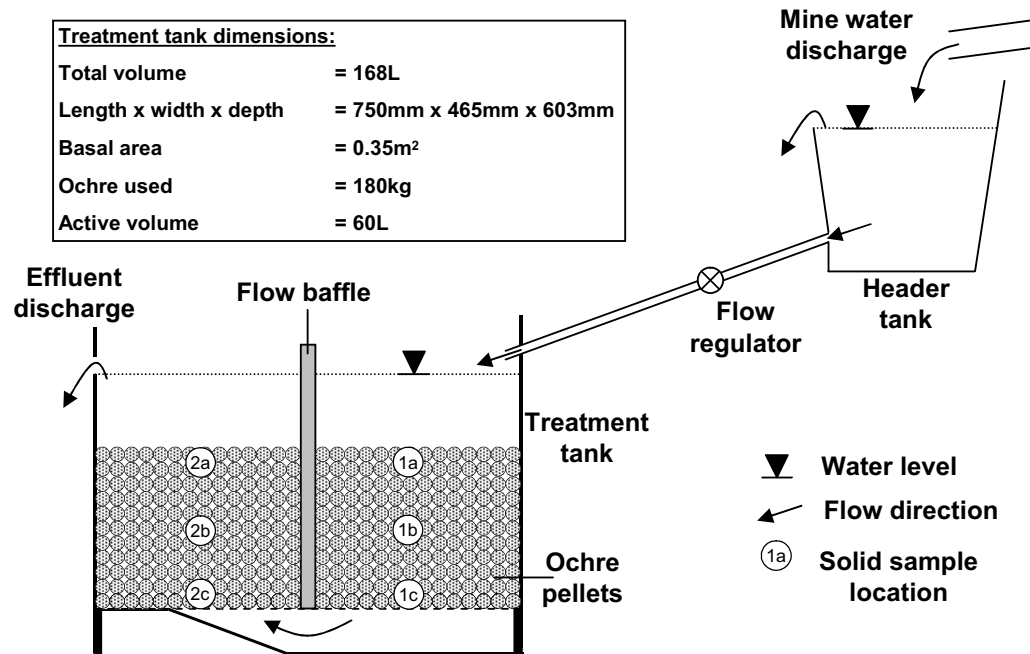
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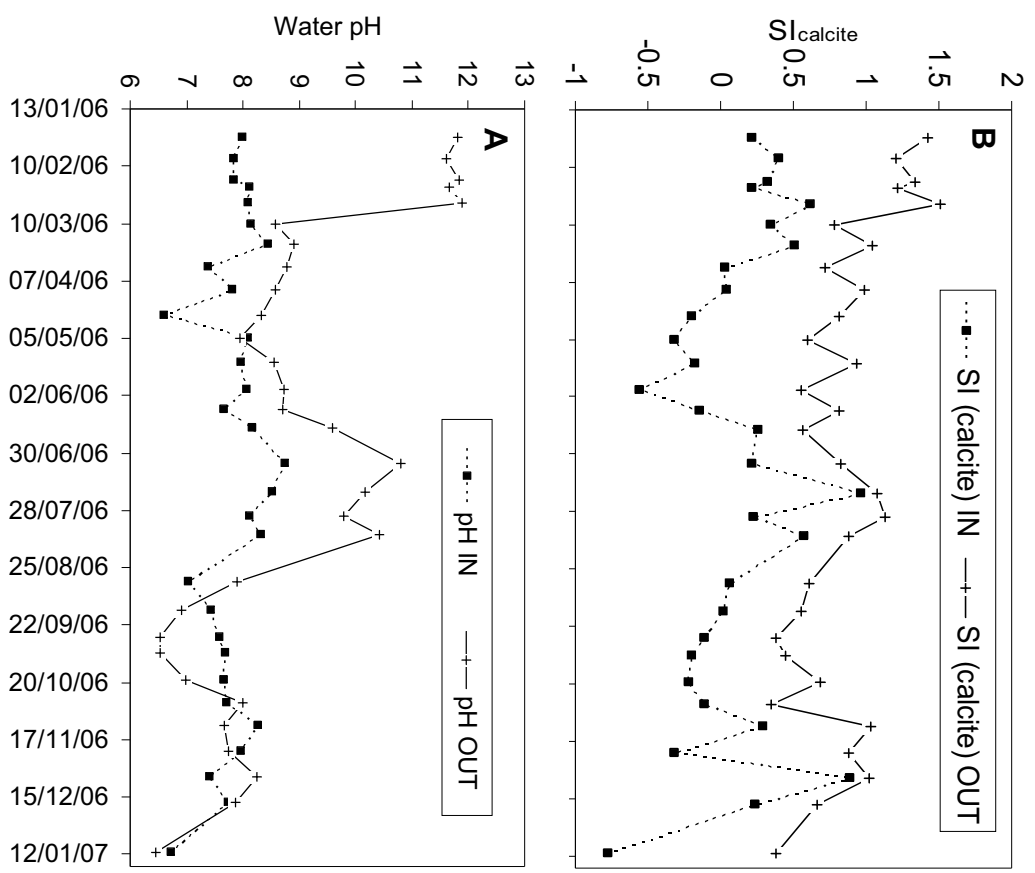
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1.23

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Figure 1





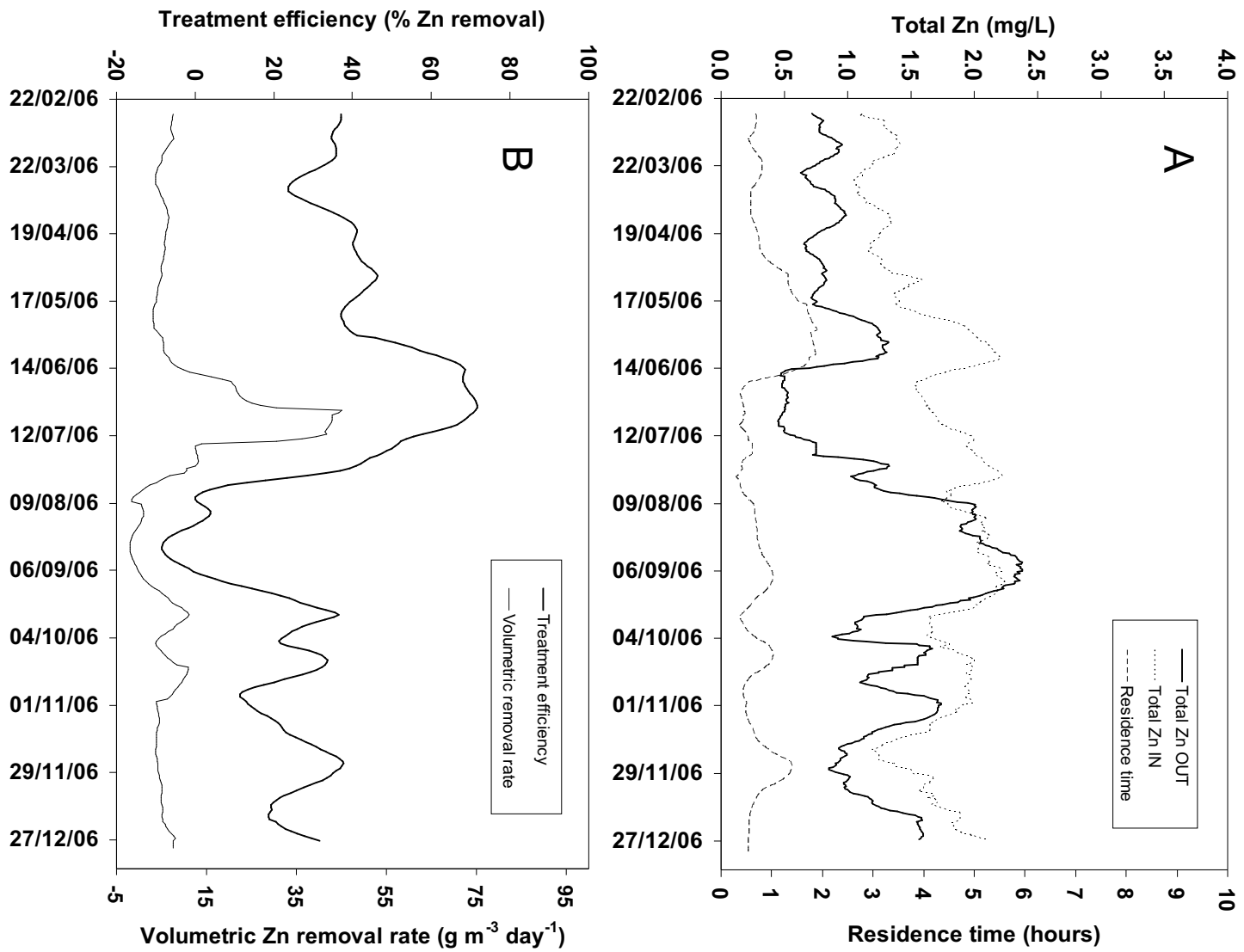


Figure 4

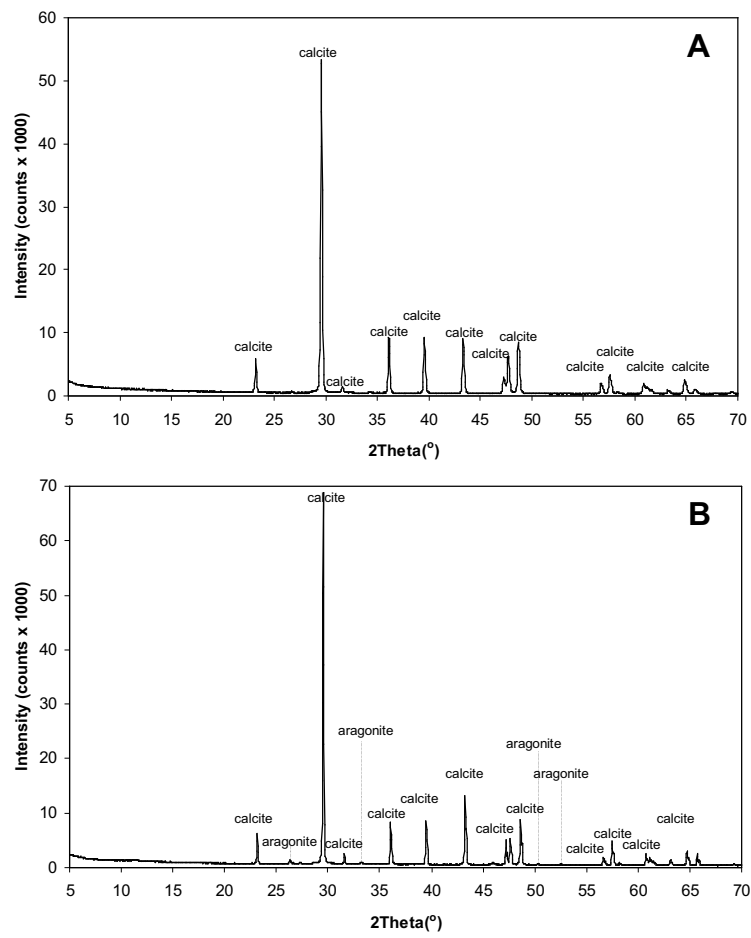


Figure 5

